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ESR and optical absorption studies on certain copper complexes

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(Plate—1)

ESR and optical absorption studies are made in the four copper complexes: 1. Copper bis-(ethylenediamine) thiocyanate, 2. Copper bis-(ethylenediamine) fluoborate, 3. Copper dipyridene thiocyanate, 4 Copper tetrapyridene fluoborate. For the first two, both single crystal and powder measurements have been made. The principal g-values are estimated from an analysis of the observations in all the complexes. A considerable covalency in the metal ligand bonding is indicated.

Introduction

ESR studies of different copper complexes with ligands such as H_2O, N_2 and O_2 etc. have been the subject of a large number of investigations (Bleaney *et al* 1949, Abe *et al* 1956, Rajan 1962, 1963, Rajan *et al* 1963). In particular, Maki *et al* (1959) and later Neimann *et al* (1961) have shown in their analysis of the ESR spectra of a number of these complexes, the importance of this method in understanding the nature of the bonding of the copper ion with its ligands. Among these complexes the ethylene-diamine derivatives are of interest, as in these the copper ions are surrounded by nitrogen atoms of ethylenediamine, resulting in a considerable covalency in the metal ligand bonding, different from that in ordinary $[Cu(H_2O)_6]^{++}$ complexes (Bose *et al* 1964, Ghosh *et al* 1965). The present work deals with measurements at room temperature on four such complexes, which have not yet been investigated. These are copper bis-(ethylenediamine) thiocyanate, $Cu(en)_2(SCN)_2$, copper bis-(ethylenediamine) fluoborate, $Cu(en)_2(BF_4)_2$, copper dipyridine thiocyanate, $Cu(py)_2(SCN)_2$ and copper tetrapyridine fluoborate, $Cu(py)_4(BF_4)_2$, for the first three of which, crystal structure data are available in literature (hereafter these will be referred to by their respective numbers given earlier). In the case of 1 and 2, single crystals as well as powder samples are studied. One advantage in each of these two crystals is that there is only one molecule in the unit cell and hence, the ESR spectra are expected to be simple without the complications that arise from the overlapping of spectra when there are two or more ions in the unit cell. An analysis of the experimental results has been attempted in terms of symmetry considerations that could be inferred from the known crystal structure. For 3 and 4 the other two substances, only powder specimens are investigated since difficulties

have been experienced in obtaining them in the form of good single crystals suitable for investigation.

Optical absorption measurements have been made on all the four substances in solution. The results are given in the following sections.

Experimental

The ESR measurements have been carried out with the spectrometer used previously by the author (1968) The optical absorption measurements have been made on a Hilger U.V.I (ultraviolet and visible) spectrophotometer in the range 350mμ to 700mμ

The complexes are prepared as in previous investigations on their crystal structure. The methods of preparation and the known crystal structures are briefly given below.

1. $Cu(en)_2(SCN)_2$

This is prepared (Bruce *et al* 1964) by the addition of stoichiometric amount of ethylenediamine to an aqueous solution of copper sulphate at room temperature. Conversion to the thiocyanate is then done by the slow addition of barium thiocyanate solution with rapid stirring and filtering off the precipitate of barium sulphate. The filtrate is vacuum dried over anhydrous calcium chloride. Violet prismatic crystals of the anhydrous compound are then obtained by slow cooling of a hot methanol solution. The crystals are tablets on (101) elongated in b direction, reported by Bruce *et al* (1964) as belonging to the triclinic system of space group $P\bar{1}$, the lattice constants being, $a = 7.352$ Å, $b = 9.364$ Å $c = 6.585$ Å, $\alpha = 86°56'$, $\beta = 113°25'$, $\gamma = 125°08'$ density $\rho = 1\ 57$ $Z = 1$.

2. $Cu(en)_2(BF_4)_2$

This has been prepared by dissolving basic copper carbonate in fluoboric acid and adding ethylenediamine Violet coloured crystals separate out. These are recrystallized from methanol solution. Single crystals of required size are obtained by slow evaporation of the solution. These are (Brown *et al* 1968) also triclinic, of space group $P\bar{1}$, with the following lattice constants. $a = 7.42$ Å, $b = 8\ 22$ Å, $c = 5\ 92$ Å, $\alpha = 100°54'$, $\beta = 105°12'$, $\gamma = 106°00'$, $\rho = 1.84$ $Z = 1$

3. $Cu(py)_2(SCN)_2$

Green coloured copper dipyridine thiocyanate, insoluble in water, is obtained by the reaction of copper sulphate with potassium thiocyanate and pyridine (Encyclopedia of Chemical Reactions. Vol III, Article II 1285, 1949). According to Porai-Koshits *et al* (1959) the crystals are monoclinic and belong to the space group C_2/m with two molecules in the unit cell.

4. $Cu(py)_4(BF_4)_2$.

The preparation of this sample given by Ibers (1953) is similar to the fluoborate, the ethylene diamine having been replaced by pyridine. A fine deep blue crystalline substance is obtained and it is purified by recrystallization from ethanol solution. Although for this compound detailed crystal data are not available a morphological study reported by Ibers indicates an orthorhombic bypyramidal type of structure of space group $P2_12_12_1$, there being four molecules in the unit cell.

Results

A (1) *Single crystals of* 1 *and* 2

The ESR observations on single crystals could be taken only on the first two compounds. In both these triclinic crystals, a set of orthogonal axes, a^*, b^*, c^* have been chosen in order to facilitate the evaluation of the g-tensor from experimental observations. These are related to the crystallographic axes a, b and c as follows : $c^* = c$, b^* axis is in the bc plane and perpendicular to the c-axis, a^* is perpendicular to $b^*c^*(= bc)$ plane. The angular variation of the ESR spectrum is studied in the planes, $b^*c^*(= bc)$ and a^*b^* (a plane perpendicular to c-axis) and ac plane. The angular variations of g^2 in the a^*b^* and b^*c^* planes in the first (1) and second (2) crystal, respectively, are shown in figures 1 and 2.

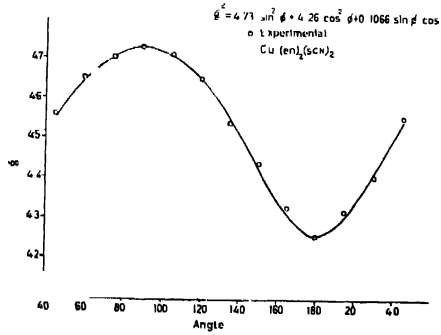

Figure 1. g^2 variation in $Cu(en)_2(SCN)_2$ in a^* b^* plane.

As the crystals contain one molecule in the unit cell, a simple direct method is adopted for the calculation of the g-tensor, as was done in the case of dibarium copper formate tetrahydrate (Ramasubba Reddy *et al* (1957), which also crystallizes in the triclinic system and contains only one molecule in the unit cell. This

procedure is based generally on those developed earlier by Pryce (1950), Weil *et al* (1958) and by Bose *et al* (1964).

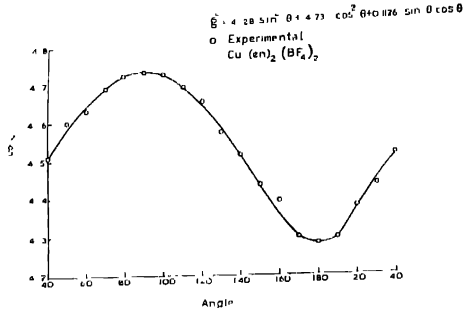

Figure 2 g^2 variation in $Cu(en)_2(BF_4)_2$ in b^* c^* plane.

If l_1, l_2 and l_3 are the direction cosines of the magnetic field with respect to a^*, b^* and c^* axes, we have,

$$g^2 = \sum_{ij=1,2,3} A_{ij} l_i l_j = A_{11} l_1^2 + A_{22} l_2^2 + A_{33} l_3^2 + 2A_{12} l_1 l_2 + 2A_{23} l_2 l_3 + 2A_{31} l_3 l_1 \quad \ldots (1)$$

where A_{ij}'s are the components of the g^2-tensor (symmetric) in the $a^*b^*c^*$ system. When these coefficients are known, the principal g-values are found by diagonalizing the matrix A. The three roots of the secular equation

$$\det [A - \lambda I] = 0 \quad \ldots (2)$$

are the squares of the principal g-values

In b^*c^* plane, if θ is the angle between the magnetic field and c^*-axis, then

$$l_1 = 0, l_2 = \sin\theta \quad l_3 = \cos\theta$$

and the above equation simplifies to

$$g^2 = A_{22} \sin^2\theta + A_{33} \cos^2\theta + 2A_{23} \sin\theta \cos\theta \quad \ldots (3)$$

The g^2 values along $c^* = c$ axis and b^* axis gives A_{33} and A_{22}. A_{23} is obtained by the least square fit method from the above equation (3). The values obtained in the two crystals 1 and 2 are

$A_{22} = 4.26$ $A_{33} = 4.26$ $A_{23} = 0.05299$ for 1

$A_{22} = 4.28$ $A_{33} = 4.73$ $A_{23} = 0.0563$ for 2

In the $a^*\,b^*$ plane if ϕ is the angle between the magnetic field and the b^* axis then

$$I_1 = \sin\phi,\ I_2 = \cos\phi \quad I_3 = 0$$

so that

$$g^2 = A_{11}\sin^2\phi + A_{22}\cos^2\phi + 2A_{12}\sin\phi\cos\phi \qquad \ldots\ (4)$$

The values A_{22} is taken from $b^*\,c^*$ plane. A_{11} is obtained from the g^2-value along a^* axis. As in the $b^*\,c^*$ plane the value of A_{12} is obtained by least square fit method using the equation (4). This gives

$$A_{11} = 4.73 \qquad A_{12} = 0.0533 \quad \text{for} \quad 1$$

$$A_{11} = 4.28 \qquad A_{12} = 0.0622 \quad \text{for} \quad 2$$

In the ac plane along a-axis, the expression for g^2 contains all the coefficients of which five are already known. Further the direction cosines of the a-axis with respect to a^*, b^* and c^* axes are given by (using the known crystal structure data).

$$I_3^a = \cos\beta = -0.3969 \quad I_2^a = \cos\gamma\cos(\alpha - 90) = -0.5746$$

$$I_1^a = 1 - [(I_3^a)^2 - (I_2^a)^2]^{1/2} = 0.7156^* \quad \text{for} \quad 1$$

$$I_3^a = 0.2622 \qquad I_2^a = -0.2736\ I_1^a = 0.9255^* \qquad \text{for} \quad 2.$$

Using the value of g^2 along a-axis the sixth coefficient A_{13} is obtained as

$$A_{13} = 0.2094 \text{ and } 0.2162 \text{ respectively for 1 and 2.}$$

The g^2 tensor $|A|$ with respect to the coordinte system a^*, b^*, c^* is therefore

$$A = \begin{vmatrix} (4.73-\lambda) & 0.0533 & 0.2094 \\ 0.0533 & (4.26-\lambda) & 0.0529 \\ 0.2094 & 0.0529 & (4.26-\lambda) \end{vmatrix} \quad \text{for 1,}$$

and

$$A = \begin{vmatrix} (4.28-\lambda) & 0.0622 & 0.2162 \\ 0.0622 & (4.28-\lambda) & 0.0563 \\ 0.2162 & 0.0563 & (4.73-\lambda) \end{vmatrix} \quad \text{for 2.}$$

*As is generally customary in these calculations the positive sign has been adopted. However further calculation has shown that the adoption of the negative sign does not lead to any appreciable change in the result.

The solution for λ for the resulting respective cubic equations

$$\lambda^3-13.25\lambda^2+58.3978\,\lambda-86.6274=0 \text{ for } 1$$

$$\lambda^3-13.29\lambda^2+59.2536\,\lambda-87.4252=0 \text{ for } 2.$$

give the following three g-values.

$$g_3=2\,197 \qquad g_2=2.064 \qquad g_1=2.041 \text{ for } 1$$

$$g_3=2.201 \qquad g_2=2.071 \qquad g_1=2.045 \text{ for } 2$$

In both the cases a nearly tetragonal symmetry is indicated. The difference between g_2 and g_1 in both cases is considered to be slightly greater than due to experimental error. The principal g-values are

$$g_{\parallel}=2.20 \qquad g_{\perp}=2.05 \text{ for } 1$$

$$g_{\parallel}=2.20 \qquad g_{\perp}=2.058 \text{ for } 2.$$

The angles θ_i between the axis of symmetry and the $a^*b^*c^*$ axes are obtained from the equation

$$A_{4i}=g_{\parallel}^2\cos^2\theta_i+g_{\perp}^2\sin^2\theta_i \qquad \ldots \quad (5)$$

where $i=1, 2,$ and 3. These are given below together with the orientation of all the g_i's with respect to the chosen system (table 1).

The values of θ_{c^*} are also deduced from the respective crystal structure data of the two compounds, these are 80° and 34° respectively, in good agreement with the experimental values

Table 1 Principal g-values and their orientations with respect to the chosen axes, a^*, b^* and c^*

Substance	Principal g-values	Angle with respect to a^*	b^*	c^*
$Cu(en)_2(SCN)_2$	$g_3=2.197$	24°36′	73°10′	71°47′
	$g_2=2.064$	72°19′	25°28′	72°13′
	$g_1=2.041$	72°36′	70°38′	−26°31′
	$g_\perp=2.05$			
	$g_{\parallel}=2.20$			75°00′
				(80°)+
$Cu(en)_2(BF_4)_2$	$g_3=2\,201$	67°54′	76°52′	24°58′
	$g_2=2\,071$	72°00′	24°58′	74°46′
	$g_1=2.045$	28°58′	70°36′	69°29′
	$g_\perp=2.058$			
	$g_{\parallel}=2.20$			35°15′
				(34°)+

(+) Values obtained from crystal structure data.

(2) *The powder*

ESR absorption of crystalline powder samples of the above two compounds has shown asymmetry in the line shape, as may be seen from figures 3(I) and 3(II) (Plate 1). The shapes are similar to those obtained by Kneubuhl (1960) in substances with two principal g-values $g_{\|}$ and $g_{\perp}$. The following values are deduced from the derivative tracings

	$Cu(en)_2(SCN)_2$	$Cu(en)_2(BF_4)_2$
$g_{\|}$	2.19	2.20
$g_{\perp}$	2.03	2.07

3) *Optical absorption studies*

Optical absorption of these two substances in aqueous solution of 0.01 percent has given two distinct peaks in each (figures 4 and 5) at the following wave numbers.

$Cu(en)_2(SCN)_2$	$Cu(en)_2(BF_4)_2$
18018 cm^{-1}	18691 cm^{-1}
17094 cm^{-1}	17857 cm^{-1}

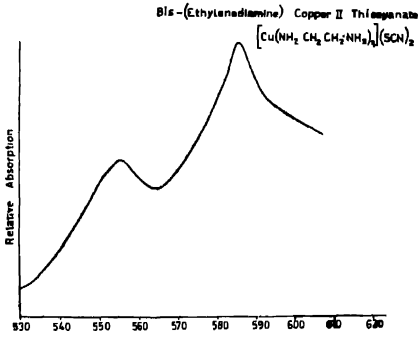

Figure 4. Optical absorption spectrum of $Cu(en)_2(SCN)_2$.

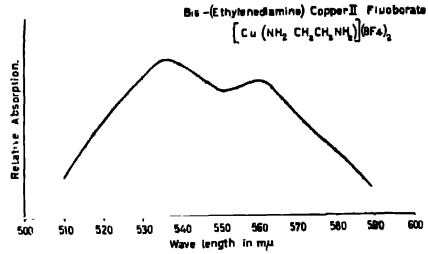

Figure 5. Optical absorption spectrum of $Cu(en)_2(BF_4)_2$.

From these absorption frequencies the covalency reduction factors are obtained using the following expressions of Bose *et al* (1965) and of Ghosh *et al* (1967) and of Pal *et al* (1968).

$$g_{\parallel} = 2\left\{1-\frac{4R'_{\parallel}K_{\parallel}'\lambda}{(E_3-E_1)} - \frac{R^2\lambda^2}{2(E_2-E_1)^2} - \frac{2R_{\perp}R'_{\perp}K'_{\parallel}\lambda^2}{(E_2-E_1)(E_3-E_1)}\right\}$$

$$g_{\perp} = 2\left\{1-\frac{R_{\perp}K_{\perp}\lambda}{(E_2-E_1)} - \frac{R_{\perp}\lambda^2(R_{\perp}-R_{\parallel}K_{\perp})}{2(E_2-E_1)^2} - \right. \qquad \ldots (6)$$

$$\left. -\frac{2R_{\parallel}^2\lambda^2}{(E_3-E_1)^2} - \frac{R_{\parallel}\lambda^2(R_{\perp}K'_{\perp}-R'_{\perp}K_{\perp})}{(E_2-E_1)(E_3-E_1)}\right\}$$

where λ is taken as -828 cm^{-1} for copper and $R_{\parallel}$, $R_{\perp}$ and $K_{\parallel}$, $K_{\perp}$ are spin orbit and orbital reduction factors respectively, arising out of the covalency effect in the metal ligand bonding. (E_2-E_1) and (E_3-E_1) are the ligand field splittings.

The parameters appearing in the above expressions are $R_{\parallel}R'_{\parallel}$ $R_{\perp}R'_{\perp}$, $K_{\parallel}K'_{\parallel}$ and $K_{\perp}K'_{\perp}$ and simplifying approximations are made which make very little difference in the ultimate calculations. Since the primed and unprimed parameters appear in the third order expressions for $g_{\parallel}$ and $g_{\perp}$, the covalency reduction factors associated with the matrix elements between the two $d(\tau)$ orbitals and that between $d(\tau)$ and $d(\rho)$ orbitals are the same: $d(\tau)$ and $d(\rho)$ are the atomic orbitals (d_{xy}, d_{yz}, d_{zx}) and ($d_{3z^2-r^2}$, $d_{x^2-y^2}$) where the quantities given in the brackets are the five degenerate states of the free ion. Therefore $R_{\parallel} = R'$ *etc.*

In this case much simplication can be made due to the fact that from ESR and optical absorption data only the products of $R_{\parallel}K_{\parallel}$ and $R_{\perp}K_{\perp}$, but not the individual quantities, are obtained Therefore the above expressions can be written by neglecting all the terms except the first two and they are as follows

$$g_{\parallel} = 2\left[1-\frac{4R_{\parallel}K_{\parallel}\lambda}{(E_3-E_1)}\right]$$

$$g_{\perp} = 2\left[1-\frac{R_{\perp}K_{\perp}\lambda}{(E_2-E_1)}\right] \qquad (7)$$

The values of $R_{\parallel}K_{\parallel}$ and $R_{\perp}K_{\perp}$ for the two crystals are given below. The results indicate a considerable covalency in the metal ligand bonding.

	$Cu(en)_2(SCN)_2$	$Cu(en)_2(BF_4)_2$
$R_{\parallel}K_{\parallel}$	0 52	0.54
$R_{\perp}K_{\perp}$	0,54	0.64

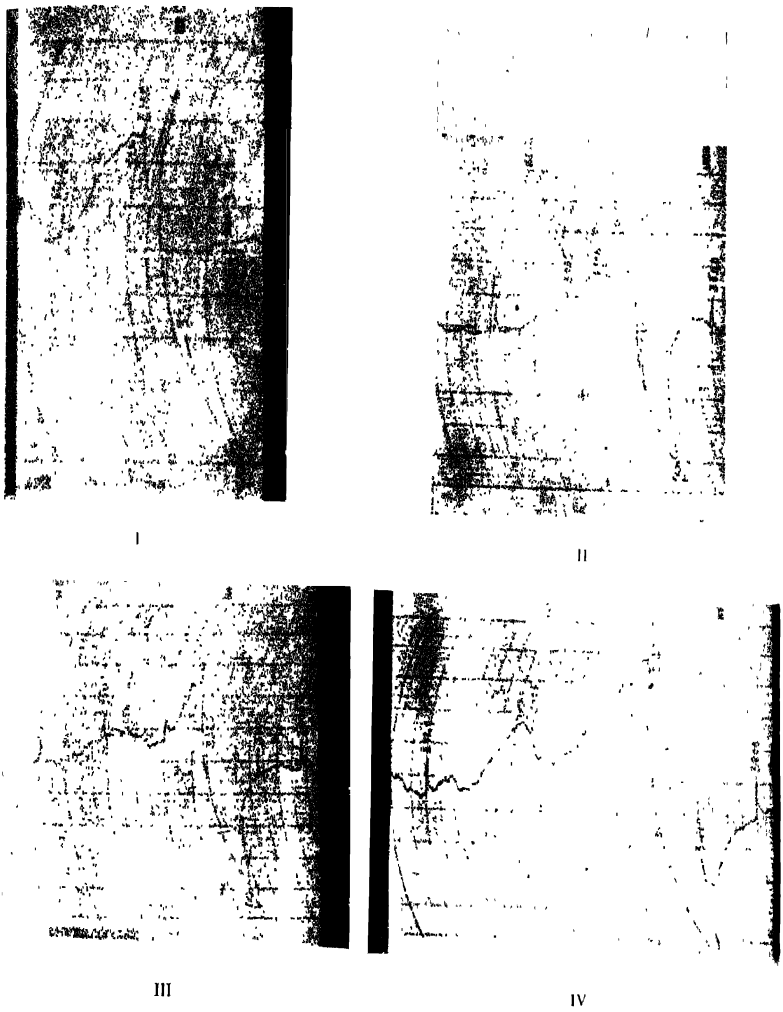

Figure 3. Derivative tracings of powder samples
I. Cu $(en)_2$ $(SCN)_2$, II. Cu $(en)_2$ $(BF_4)_2$, III. Cu $(Py)_2$ $(SCN)_2$ and
IV. Cu (Py_4) $(BF_4)_2$

B. *Powder patterns of* 3 *and* 4

The derivative curves obtained for the powder specimens of the two pyridine compounds are also shown in figures (3) and (4). The respective principal g-values that are deduced and the absorption frequency in the case of $Cu(py)_4(BF_4)_2$ together with the estimated value of the covalency factor, are given below for $Cu(py)_2(SCN)_2$ no clear absorption peak has been observed.

Since only one peak is obtained in the absorption in 4, the RK value is estimated by taking the average g-value and using the approximate equation

$$g_{av} = \left(\frac{g_{\parallel}^2 + 2g_{\perp}^2}{3}\right)^{1/2} = 2 - \frac{4\lambda RK}{\Delta E} \qquad \ldots (8)$$

where the following approximations have been made : $R_{\parallel}K_{\parallel} \approx R_{\perp}K_{\perp} \approx RK$ which is strictly valid when π-bonding is neglected, and $E_2 - E_1 \approx E_3 - E_1 \approx \Delta E$

3. $Cu(py)_2(SCN)_2$	4. $Cu(py)_4(BF_4)_2$
$g_{\parallel} = 2.28$	$g_{\parallel} = 2.30$
$g_{\perp} = 2\ 02$	$g_{\perp} = 2.02$
	$\Delta E = 14493\ cm^{-1}$
	$RK = 0.54$

As in the first two compounds, the RK value indicates considerable covalency in the metal ligand bonding in $Cu(py)_4(BF_4)_2$. But the value may be considered to be only approximate

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